

Comparative Disappearance of Dioxathion,
Malathion, Oxydemetonmethyl and Dialifor from
Florida Citrus Leaf and Fruit Surfaces

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Comparative Disappearance of Dioxathion, Malathion, Oxydemetonmethyl and Dialifor from Florida Citrus Leaf and Fruit Surfaces¹

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Abstract. Surface residue disappearance rates of dioxathion, malathion, oxydemetonmethyl, and dialifor were the same for fruit and leaves, and they increase with temperature. Disappearance rates were in the order of malathion $\geq$ oxydemetonmethyl $\gg$ dialifor $\geq$ dioxathion. Malaoxon was present in relatively constant amounts under dry, cool, clear conditions but was not detected under wet, hot, cloudy conditions.

The disappearance rate of organophosphate insecticides is a prime consideration for worker safety reentry times, treatment to harvest intervals, and pest management practices. Comparison of the residue behavior of different organophosphates is one approach for the prediction of their environmental fate (Freed *et al.* 1979). The purpose of this study was to examine simultaneously the rate of disappearance of four organophosphates in each of two environments.

Materials and Methods

The experimental grove was a 15-year-old Valencia orange grove on rough lemon rootstock. Trees were uniform in height, in canopy density, and in excellent horticultural condition. This grove belongs to the University of Florida and all pest management decisions are made by the authors. Experimental plots were four trees each. Treatments were repeated four times in a random block design with no-spray plots included as controls. Treatments were applied with a truck-mounted high-pressure sprayer equipped with Bean trigger guns at 600 psi. Dioxathion (8E) (S,S-1,4-dioxane-2,3-diyl bis (O,O-diethyl phosphorodithioate), oxydemetonmethyl (2L) S-[2-(ethylsulfinyl) ethyl] O,O-dimethyl phosphorothioate, dialifor (4E) S-[2-chloro-1-(1,3-dihydro-1,3-dioxo-2H-isindol-2-yl) ethyl] O,O-diethyl phosphorodithioate, and malathion (9.5E) (Diethyl mercaptosuccinate, S-ester with O,O-dimethyl phosphorodithioate) were applied at a rate of 1.58 g AI/ha (4 lb AI/acre in 750 gal of water/acre). Both experiments were carried out on the same plots. Experiment 1 was conducted from March 14-April 11, 1979 and Experiment 2 from July 11-August 9, 1979.

Forty leaves per replicate were punched at random directly into a leaf punch jar and dislodge-

¹ Florida Agricultural Experiment Stations Journal Series No. 2098.

able residues were processed according to Iwata *et al.* (1977). Ten fruit per plot were clipped into 2.5 gal pickle jars in the field. Fruit were rolled twice in the same pickle jar at 70 rpm for 5 min in 200 ml of Sur-Ten solution to obtain dislodgeable residues. Two 20 ml methylene chloride and two 40 ml methylene chloride extractions were made to recover materials from leaf and fruit washes, respectively. Recoveries from fortified ($0.10 \mu\text{g}/\text{cm}^2$) 40-leaf punch washes were: malathion $89 \pm 2\%$; malaoxon² $95 \pm 5\%$; dialifor $84 \pm 6\%$; oxydemetonmethyl $97 \pm 2\%$; and dioxathion $80 \pm 3\%$. The results were not corrected for recoveries. Dioxathion, oxydemetonmethyl, and dialifor were analyzed at 210°, 190°, and 230°C, respectively, on a 0.8 m, 2 mm id silanized glass column packed with 10% DC-200 + 1.5% QF-1 on 80-100 mesh Chromosorb W(HP). This packing material was a gift of Dr. J. S. Thornton, Mobay Chemical Corp., Kansas City, MO. Detection was with a nitrogen-phosphorous detector in a Hewlett-Packard 5730A gas chromatograph. Other conditions were: He, 30 ml/min, injection port 250°C, detector 200°C. Malathion was analyzed on a 0.8 m silanized 2 mm id glass column packed with 5% SP 2100 on 100-120 mesh GasChrom Q; operating conditions of the Tracor 550 GC were: Column temperature 180°C, injection port 210°C, flame-photometric detector 180°C, N_2 40 ml/min. Oxydemetonmethyl was oxidized to the sulfone prior to gas chromatography according to the method of Thornton *et al.* (1977).

Analytical standards of dioxathion and dialifor were provided by Hercules, Inc., Wilmington, DE. Malathion and malaoxon standards were provided by American Cyanamid Corp., Princeton, NJ; oxydemetonmethyl and oxydemetonmethyl sulfone by Mobay Chemical Corp., Kansas City, MO.

Rainfall, temperature, and leaf wetness monitoring have been reported (Nigg *et al.* 1977). Solar radiation monitoring was previously described (Nigg *et al.* 1979). Residue concentration versus time is presented on a ln-ln basis according to Stamper *et al.* (1979) and Nigg and Stamper (1980). Errors (rms) in B are calculated according to Baird (1962)

$$\Delta B = [(1-R^2) \text{var}(Y^{\text{obs}})/(n-2) \text{var}(X)]^{1/2} \quad (1)$$

Results and Discussion

Weather differed appreciably between the two experiments. Cumulative average temperature (°C) after 29 days was 581.3 (Exp. 1) and 840.4 (Exp. 2). Cumulative RH (hr over 90%) was 336.5 (Exp. 1) and 472.5 (Exp. 2). Cumulative solar incidence ($\text{g cal cm}^{-2} \text{ min}^{-1}$) was twice as great in Experiment 1 (23,251.9) than in Experiment 2 (10,518.9). There was no rainfall in Experiment 1 but 12.71 inches during Experiment 2. Cumulative leaf wetness (hr) was 206.68 (Exp. 1) and 371.81 (Exp. 2).

In some previous studies, leaf, fruit, and soil surface residue disappearance was correlated with cumulative weather variables (Nigg *et al.* 1977, 1978, 1979). In this series of experiments, however, time alone was so similar to a weather model in explaining residue variation that only a time base was used for these data. Figure 1 illustrates the difficulty. Time correlates extremely well with each of the cumulative weather variables, and weather variables correlate with one another. It is, therefore, impossible to ascertain the relative importance of any individual weather variable to pesticide disappearance in a given experiment. Table 1 summarizes the results of the statistical analyses.

The fifth column of Table 1 tests whether significant (68% confidence level) differences exist between the B's for leaf and fruit surfaces, all other variables the same. Even at this low confidence level, which should reveal weak differences, only about one-half the differences are significant. The data, therefore, do not support a conclusion that disappearance rates, after day 1,

² Malaoxon—diethyl [(dimethoxyphosphinyl)thio] butanedioate.

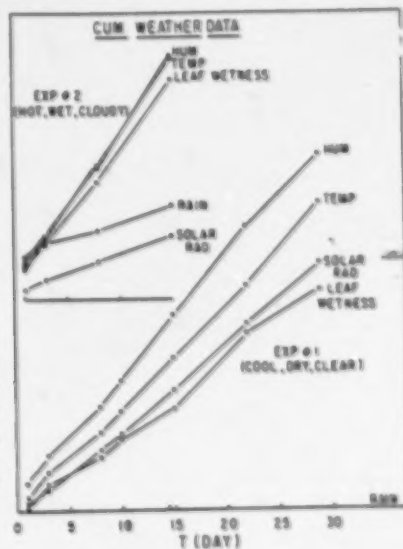


Fig. 1. Cumulative weather variables vs. time in days. Cum. Avg. Temp. ($^{\circ}\text{C}$), Cum. RH (hr over 90%); Cum. Solar Incidence ($\text{g cal cm}^{-2} \text{ min}^{-1}$), Cum. Leaf Wetness (hr); Cum. Rainfall (inches). There are no actual units given for the y-axis for comparative purposes

differ between leaf and fruit surfaces. This result agrees with previous studies (Stamper *et al.* 1979, Nigg and Stamper 1980) of other organophosphates.

For these reasons, leaf and fruit data are combined to give columns 6–8 of Table 1 and Figures 2–5, and usually resulted in increased correlations. Column 9 of Table 1 tests for significant (68% level) differences between Experiments 1 and 2. Except for dialifor, a close exception, B's in Experiment 2 are significantly higher. Probably elevations in temperature increase the disappearance rate, also in agreement with the results of previous investigations (Nigg and Stamper 1980, Nigg *et al.* 1979).

Column 7 of Table 1 indicates that the rates of disappearance of the four compounds tested are ordered: malathion $\geq$ oxydemetonmethyl $\gg$ dialifor $\geq$ dioxathion.

Diffusion theory alone predicts that after a certain time all B's should attain the value 1.5 (Stamper *et al.* 1979). Probably, in the cases of dialifor and dioxathion, particularly, sufficient time had not elapsed.

Figure 6 presents the malaoxon data for leaf and fruit surfaces in Experiment 1 (dry, cool, clear conditions). Actual residue values are noted by each point. The lines shown are the % malaoxon residue (malaoxon/malathion $\times$ 100). The actual quantity of malaoxon varied surprisingly little over the course of this experiment. In previous experiments, a rise of oxon metabolite of parathion, carbophenothion, and ethion was evident (Nigg *et al.* 1977, 1978, 1979) followed by disappearance. Since the parent compound, malathion, exhibited a steady disappearance, the percentage of malaoxon increased (Figure 6). A small production of malaoxon during the extraction process might account for these data, but no malaoxon was detected in malathion-fortified fruit and leaf washes, thus eliminating this possibility. No malaoxon was detected during Experiment 2, a wet, hot, cloudy period.

Table 1. Disappearance rates (B) from leaf and fruit surfaces (col. 2-4), and for leaf and fruit combined (col. 6-8); B determined from $\ln (C_t/C_0) = A + B \ln (t/t_0)$

Col.	1 Exp.	2 Surface	3 B $\pm$ Δ B	4 (R ²)	5 ^a B _L - B _F	6 Surface	7 B $\pm$ Δ B	8 (R ²)	9 ^a B _L - B _F
M	1	L ^b	1.17 $\pm$.12	(.95)					
A	1	F ^c	0.88 $\pm$.08	(.96)	+.29 $\pm$.14	L + F	1.03 $\pm$.08	(.97)	
L	2	L	1.18 $\pm$.51	(.84)					+.54 $\pm$.37
T	2	F	1.96 $\pm$.21	(.99)	-.78 $\pm$.55	L + F	1.57 $\pm$.36	(.95)	
H									
I									
O									
N									
OM	1	L	0.55 $\pm$.16	(.71)					
XE	1	F	0.12 $\pm$.06	(.49)	+.42 $\pm$.17	L + F	0.34 $\pm$.08	(.77)	
YT	2	L	1.11 $\pm$.07	(.99)					+.99 $\pm$.08
DH	2	F	1.55 $\pm$.07	(.99)	-.45 $\pm$.10	L + F	1.33 $\pm$.00	(.99)	
EY									
ML									
E									
T									
O									
N-									
D	1	L	0.38 $\pm$.06	(.89)					
I	1	F	0.50 $\pm$.09	(.86)	-.11 $\pm$.11	L + F	0.44 $\pm$.06	(.90)	
A	2	L	0.57 $\pm$.11	(.94)					+.15 $\pm$.16
I	2	F	0.60 $\pm$.21	(.80)	-.02 $\pm$.23	L + F	0.59 $\pm$.15	(.89)	
F									
O									
R									
D	1	L	0.38 $\pm$.09	(.82)					
I	1	F	0.30 $\pm$.06	(.86)	+.08 $\pm$.11	L + F	0.34 $\pm$.06	(.88)	
O	2	L	0.51 $\pm$.17	(.82)					+.20 $\pm$.16
X	2	F	0.57 $\pm$.19	(.82)	-.06 $\pm$.25	L + F	0.54 $\pm$.15	(.87)	
A									
T									
H									
I									
O									
N									

^a Cols. 5 and 9 test for significant (68% confidence level) differences between leaf vs. fruit and Exp. 1 vs. Exp. 2, respectively

^b Leaves

^c Fruit

Conclusions

Fruit and leaf surface organophosphate residue data are so similar that only one type of sample is necessary for worker reentry residue data after the initial concentrations are determined. Leaf samples are much more convenient to

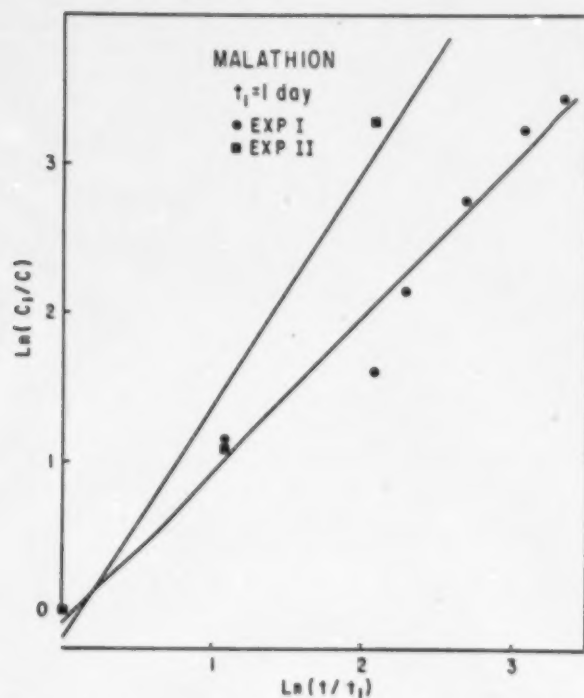


Fig. 2. Ln-Ln plot of combined malathion fruit and leaf surface residues. Initial concn (day 1) of malathion fruit $0.4 \pm 0.1 \mu\text{g}/\text{cm}^2$ Exp. 1, leaves $0.5 \pm 0.2 \mu\text{g}/\text{cm}^2$ Exp. 1; fruit $0.006 \pm 0.002 \mu\text{g}/\text{cm}^2$ Exp. 2, leaves $0.006 \pm 0.003 \mu\text{g}/\text{cm}^2$ Exp. 2

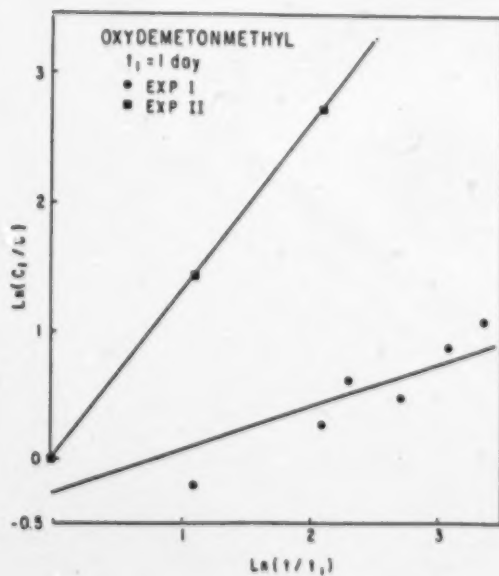


Fig. 3. Ln-Ln plot of combined oxydemetonmethyl fruit and leaf surface residues. Initial concn (day 1) of oxydemetonmethyl fruit $0.5 \pm 0.03 \mu\text{g}/\text{cm}^2$ Exp. 1, leaves $0.2 \pm 0.02 \mu\text{g}/\text{cm}^2$ Exp. 1; fruit $0.005 \pm 0.002 \mu\text{g}/\text{cm}^2$ Exp. 2, leaves $0.003 \pm 0.002 \mu\text{g}/\text{cm}^2$ Exp. 2

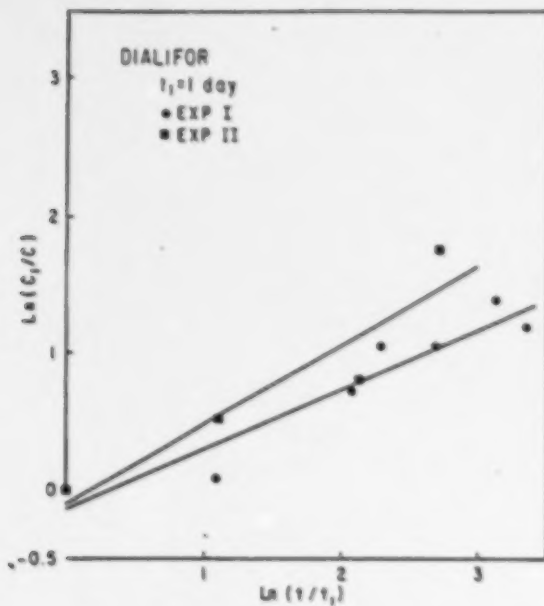


Fig. 4. Ln-Ln plot of combined dialifor fruit and leaf surface residues. Initial concn (day 1) of dialifor fruit $1.1 \pm 0.3 \mu\text{g}/\text{cm}^2$ Exp. 1, leaves $0.6 \pm 0.08 \mu\text{g}/\text{cm}^2$ Exp. 1; fruit $0.2 \pm 0.05 \mu\text{g}/\text{cm}^2$ Exp. 2, leaves $0.1 \pm 0.02 \mu\text{g}/\text{cm}^2$ Exp. 2

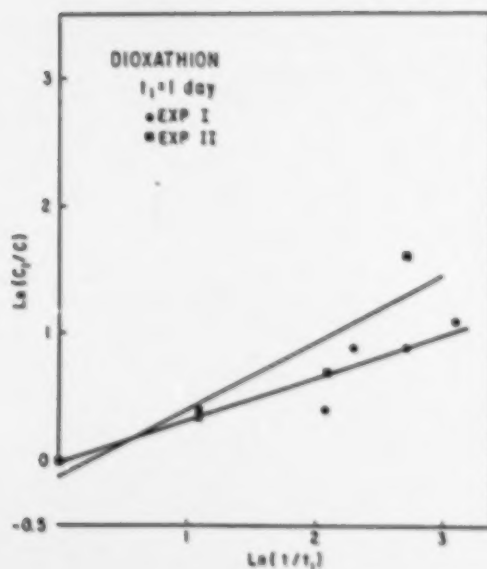


Fig. 5. Ln-Ln plot of combined dioxathion fruit and leaf surface residues. Initial concn (day 1) of dioxathion fruit $0.6 \pm 0.1 \mu\text{g}/\text{cm}^2$ Exp. 1, leaves $0.3 \pm 0.03 \mu\text{g}/\text{cm}^2$ Exp. 1; fruit $0.06 \pm 0.03 \mu\text{g}/\text{cm}^2$ Exp. 2, leaves $0.04 \pm 0.02 \mu\text{g}/\text{cm}^2$ Exp. 2

process and extract compared to fruit (Gunther *et al.* 1977, Iwata *et al.* 1977) and the behavior of both types of residue sample is essentially the same.

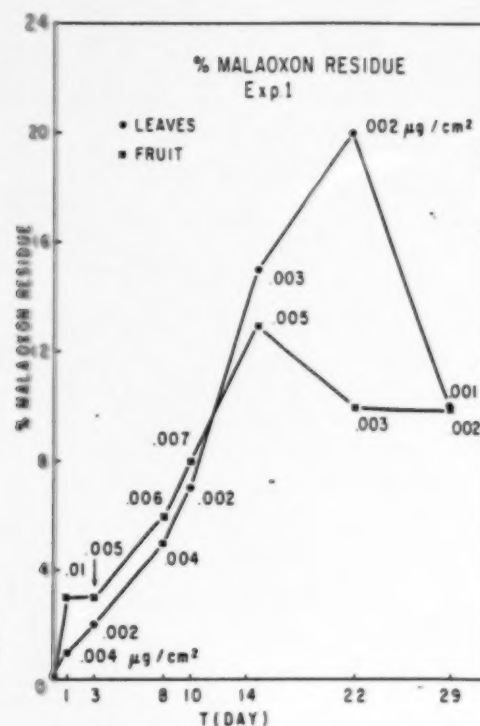


Fig. 6. % malaoxon residue. Malaoxon/Malathion $\times 100$. Actual values are next to each point in $\mu\text{g}/\text{cm}^2$.

Elevated temperatures appeared to enhance the disappearance of surface residues.

We suggest that the physical properties of pesticides, such as diffusion coefficient and/or vapor pressure, each temperature dependent, may account for our observed differences in disappearance rates.

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